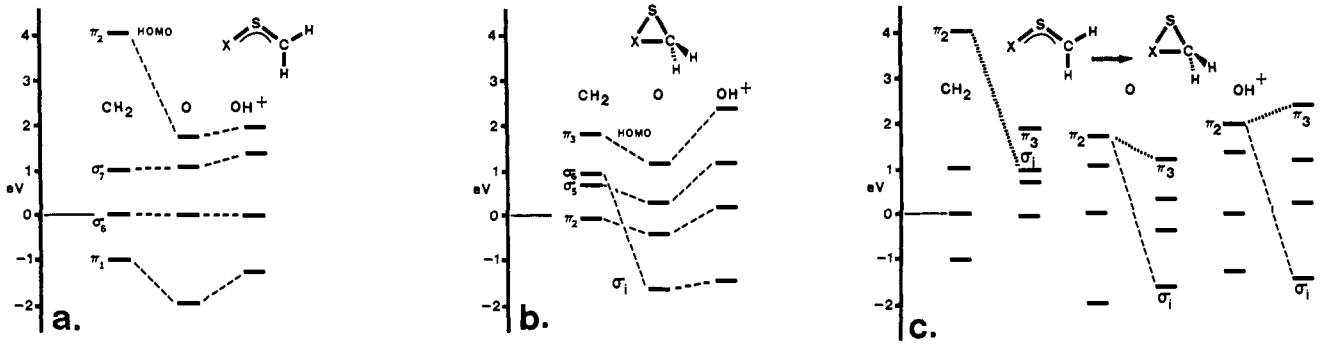


Figure 2. Relative molecular orbital energies of **3** and **4** (the energies of the σ_6 MO's have been arbitrarily equated to zero in Figure 2a, the levels in Figure 2b and c are on the same scale): (a) the open series; (b) the closed series; (c) ring closure. For (a) and (b) the dotted lines connect orbitals of comparable symmetry.[19] For (c) ||||||||||| corresponds to the actual correlation; ------ corresponds to a permissible but avoided correlation.

nificant alteration in this case is the energy lowering of the MO associated with the in-plane sulfur lone pair, σ_i. Again relative increasing localization of electron density on atom X can be considered a critical factor in the level stabilization.

Thus by replacing carbon with oxygen the π_{HOMO} of **3** and the σ_i lone-pair orbital of **4** drop significantly in energy. The remaining MO's are essentially unaffected. The consequence of these changes for the ring closure process is shown in Figure 2c. Analogous to the behavior of the well-studied symmetrical and isoelectronic allyl anion,[17] thiocarbonyl ylide **3a** is transformed to episulfide **4a** while the high-lying occupied orbitals connect by means of a π_{HOMO}–σ_i correlation. By contrast thioformaldehyde *S*-oxide (**3b**) and its conjugate acid **3c** ring close by taking advantage of a π_{HOMO}–π_{HOMO} correlation. The π_{HOMO}–σ_i interaction is avoided here presumably on energy grounds (Figure 2c).

The existence of a facile ring closure route for thiocarbonyl *S*-oxides has obvious implications for the reverse process. The oxathiirane ring can, in principle, open by electrocyclic cleavage of either the C–O or the C–S bond to produce a sulfine or the corresponding keto sulfide, respectively. The latter reaction has been investigated numerically and found to mimic the former in its essential mechanistic features. The presently unknown keto–sulfide system thus may intervene between thiocarbonyl *S*-oxide and product carbonyl. Of significance is the implication that unsymmetrical heterosubstituted sulfur-containing three-membered rings possess an attractive, relatively low energy mechanism for sulfur extrusion not involving the expulsion of a sulfur atom from the oxathiirane ring. By contrast episulfides do not possess a similar ground state mechanistic alternative for cleavage of the C–S bond.[18]

An important general point arising from these observations is that the introduction of strong asymmetric perturbations, for example, hetero atoms, into a carbon framework can lead to severe reordering of energy levels. In addition electron distribution may be shifted to such an extent relative to the symmetrical model that symmetry restrictions on orbital interactions are lifted. Concerted reactions can, in principle, then proceed with level correlations quite distinct from those derived by considering an all carbon backbone alone. Any of several orbital correlations[19] may be employed by the system under consideration, the determinant being the combination of lowest energy. By contrast it must be emphasized that symmetrical species such as **3a** and **4a** are constrained to orbital interactions governed by the widely applied orbital symmetry conservation principle.[17a]

Acknowledgments. We are grateful to Dr. Ulrich Mueller-Westerhoff (IBM Corporation) for helpful advice and to Dr. Russell Boyd (University of British Columbia) for encouragement and counsel. Partial financial assistance was generously provided by the Carlsbergfond (Copenhagen); computer facilities were by NEUCC-Denmark.

(17) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 14, 370 (1969); M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4291 (1971), and references therein.

(18) R. Hoffmann, C. C. Wan, and V. Veagu, *Mol. Phys.*, **19**, 113 (1970); O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **94**, 8317 (1972).

(19) The introduction of a strong perturbation naturally prevents a rigorous description of the reaction pathway in terms of symmetry elements alone. In some cases, however, pseudo-symmetry is maintained. In others only a careful stepwise analysis of MO coefficients between potential surface minima permit an orbital correlation to be established.[20]

(20) The interplay of energy and symmetry considerations obtains for a wide variety of heteroelectrocyclic processes and will be reported shortly; J. P. Snyder and B. Schilling, unpublished work.

(21) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1971–1976.

James P. Snyder[21]
Department of General and Organic Chemistry
University of Copenhagen
2100 V Copenhagen, Denmark
Received March 12, 1974

Stereospecific Solid-State Rearrangement of 1,2,5,6-Tetracyano-*anti*-tricyclo[4.2.0.0^{2,5}]octane to 1,2,5,6-Tetracyano-(*Z*,*E*)-cycloocta-1,5-diene[1]

Sir:

Strict application of orbital symmetry rules[2] to the thermal cleavage of the middle cyclobutane ring of tricyclo[4.2.0.0^{2,5}]octanes, **1**, predicts the formation of (*Z*,*E*)-cycloocta-1,5-dienes, **2**, by the ($\sigma 2_s + \sigma 2_a$) pathway. However, only the (*Z*,*Z*)-isomers **3a** and **3b** were

(1) A preliminary report of part of this work was presented by one of us (D. B.) at the 3rd International Symposium on Synthesis in Organic Chemistry, Oxford, July 1973.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

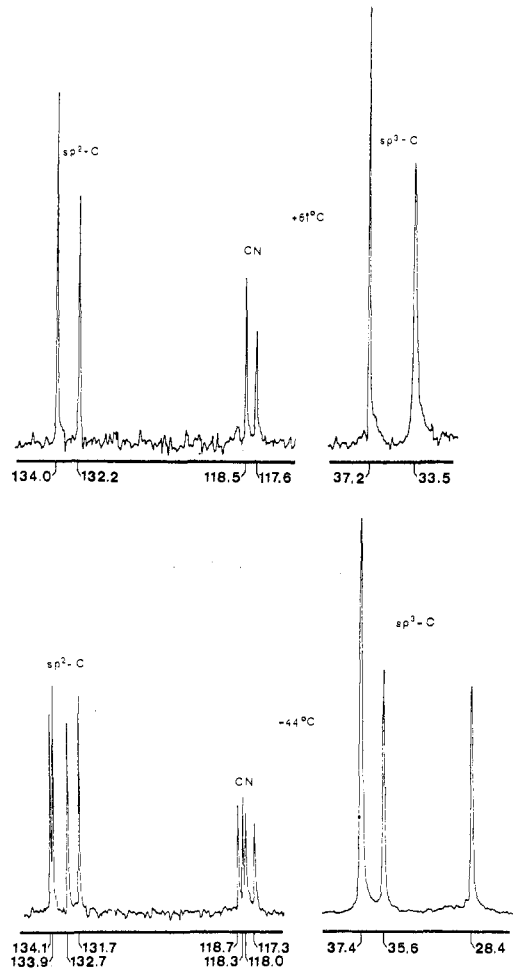
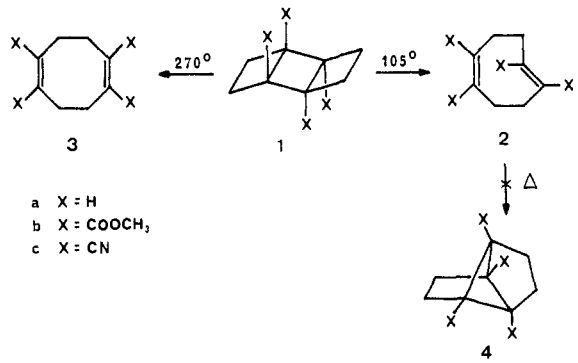


Figure 1. Proton noise decoupled ^{13}C nmr spectra of 1,2,5,6-tetracyano-(*Z,E*)cycloocta-1,5-diene (**2c**) at +61 and −44° (15% solution in CD_3NO_2). The shift scale is in parts per million downfield from internal TMS.

isolated after thermolyses of the parent hydrocarbon **1a**[3] and the tetraester **1b**.[4] We now wish to report the exclusive thermal isomerization of tetranitrile **1c** to the (*Z,E*)-cycloocta-1,5-diene **2c** in the solid state (Scheme I).

Scheme I



1c was obtained by irradiation of an acetonitrile (400 ml) solution of 1,2-dicyanocyclobutene[5,6] (10.2 g) and benzophenone (0.5 g) with a 125-W Hg arc through a Pyrex filter. Filtration of the precipitate yielded 9.3 g (91%) of **1c** as white crystals: mp 182°; *m/e* 208 M^+; $\nu_{C\equiv N}$ 2233 cm^{-1}.[7] The anti configuration of **1c** was confirmed by a low resolution survey X-ray analysis.[8]

Attempted vacuum sublimation of **1c** at 165° gave a white sublimate and a crystalline brown residue, which after 30 min no longer contained **1c**. The sublimate proved to be pure (*Z, E*)-isomer **2c** (42% yield; mp 192–193°)[7] by its chemical reactions (*vide infra*) and temperature-dependent ^{13}C nmr spectra (Figure 1). At −44°, all the sp and sp^2, and two of four sp^3 carbons give separate signals. At +61°, the reduced number of bands shows convincingly the existence of a flipping process in **2c**, similar to that discussed for **2a**.[9]

From the residue obtained after heating **1c** in a vacuum (*Z,Z*)-isomer **3c** (48% yield; mp 230–231°; δ 3.0 ppm (s))[7] was isolated after crystallization from acetonitrile. The proton noise decoupled ^{13}C nmr spectrum of **3c** shows three signals at 29.2 (sp^3 carbons), 117.2 (cyano sp carbons), and 127.9 ppm (sp^2 carbons), respectively, unsplit down to −40°.[10]

This first result provoked efforts to show irrevocably that the (*Z,E*)-isomer is the primary product of the kinetically controlled 2 + 2 cycloreversion of **1c**. Unfortunately, the very low solubility of **1c** in all conventional solvents does not allow experiments in solution. However, in the crystalline state at about 100° very clean isomerization of **1c** to **2c** takes place; *e.g.*, after heating **1c** to 105° for 72 hr **2c** is obtained in 96% yield with only traces (tlc) of **3c**. *This is the first example of stereospecific cleavage of an anti-tricyclo[4.2.0.0^{2,5}]octane to an isolable (Z,E)-cycloocta-1,5-diene.* The proportion of **3c** to **2c** is increased at higher temperatures, and **3c** is the only low-molecular thermolysis product at 270° (78% yield). In order to validate the reaction sequence **1c** → **2c** → **3c**, parallel solid-state thermolyses of both **1c** and **2c** over the temperature range of 96–165° were performed. The closely similar contents of **2c** and **3c** after reactions[11] very likely rules out the direct formation of **3c** from **1c**.

After an initial period, corresponding to about 15% conversion of **1c**, good first-order kinetics of thermolysis of **1c** in the solid state was observed over the temperature range 96–131°. Least-squares calculations on the results gave the Arrhenius equation

$$\log(k_{solid}/sec^{-1}) = (15.6 \pm 1.3) - (34.9 \pm 2.3)/\theta$$

dicyanocyclobutene were determined by direct absorption in ethyl iodide and from the O–O transition in the low-temperature uv spectrum, respectively. We are very indebted to Dr. A. Braun for these measurements.

(7) Complete spectral data are available upon request.

(8) Crystals of **1c** are: triclinic; a = 6.78 (2), b = 7.73 (2), c = 6.89 (2) Å; α = 122.7 (2), β = 118.0 (2), γ = 87.3 (2)°; V = 257.2 Å^3; ρ_{calcd} = 1.34 g cm^{-3} for Z = 1. The sharpened Patterson synthesis was unequivocally interpreted in terms of a centrosymmetric anti-model. Least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms converged at R = 0.14 for 435 independent reflections ($I \geq 3\sigma(I)$). Bond lengths and angles are within the expected tolerances. See paragraph at end of paper regarding supplementary material.

(9) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **89**, 4024 (1967). For figures of two possible conformers see therein and ref 16.

(10) The ^{13}C nmr spectrum is incompatible with **4c**, a reasonable product of a thermal transannular ($\pi 2_s + \pi 2_a$) cycloaddition of the strained double bonds in **2c**. For comparison, carbon signals in **4a** appear at 26.8 and 52.2 ppm. We thank Professor R. Srinivasan cordially for providing his unpublished ^{13}C nmr data of authentic **4a**.

(11) **2c** and **3c** are conveniently separated by silica gel column chromatography with solvent system benzene–acetonitrile (80:20).

(3) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

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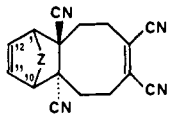
(5) D. Belluš, K. von Bredow, H. Sauter, and C. D. Weis, *Helv. Chim. Acta*, **56**, 3004 (1973).

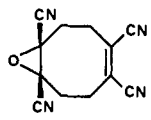
(6) E_T = 61.9 ± 1.7 kcal/mol and E_S = 114.4 ± 0.5 kcal/mol of 1,2-

where $\theta = 2.303RT$ kcal/mol. These rate constants are considerably (*e.g.*, 4×10^3 times at 100°) lower than those found for solution isomerization of 1,4-dicyanobicyclo[2.2.0]hexane,[12] the structurally most similar model compound.

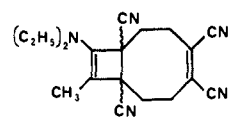
The chemical reactivity of **2c** was briefly investigated. **2c** undergoes reactions at the (*E*) double bond with cyclopentadiene or furan in acetonitrile at 20° with quantitative formation of adducts **5** (mp 259–260°) and



5 Z = CH_2
6 Z = O



7



8

6 (mp 188–189°), respectively, with trans-fused cyclooctene rings (nmr).[7] The solid-state thermolysis (105°, vacuum) of **6** is of interest insofar as only pure **2c** is formed. The absence of (*Z,Z*)-isomer **3c**, thermodynamically more stable by at least 9 kcal/mol,[13] excludes any stepwise cleavage of single bonds during the retro-Diels–Alder reaction of **6** and is, in our opinion, a striking demonstration of the concertedness of this reaction.

When solutions of **2c** are exposed to air at room temperature, epoxide **7** (mp 195–196°)[7] forms spontaneously. More convenient is oxidation of **2c** with hydrogen peroxide or *m*-chloroperbenzoic acid giving **7** in 95% yield. The inversion of configuration on one of the (*E*) double bond carbons during the oxidation was established by X-ray analysis of **7**.[14]

Treatment of **2c** in acetonitrile at −10° with 1-diethylamino-1-propyne gave **8** (mp 165–166°; ir(KBr) ν 2231 (sat. CN), 2219 (unsat. CN), 1675 cm^{-1} (C=C in cyclobutanoneenamine[15]))[7] in 62% yield. Its stereochemistry is presently unknown.

Why can the tricyclooctane **1c** isomerize exclusively to (*Z,E*)-cycloocta-1,5-diene **2c** while tricyclooctanes **1a** and **1b** apparently isomerize directly to (*Z,Z*)-cycloocta-1,5-dienes **3a** and **3b**? One reason may be that the dissociation energy of the first endocyclic single bond to be opened in **1c** is decreased by some 14.6 kcal/mol[12] because of the two bridgehead α-cyano groups. As a consequence, the difference between the activation energy for formation of the (*Z,E*) isomer and the activation energy for consecutive (*Z,E*) → (*Z,Z*) isomerization[16] may be considerably higher in the case of **1c** than the corresponding difference in the case of **1a** or even **1b**.[17] It is also not unreasonable to assume intermediate formation of **2a** and **2b** in the latter two cases followed by rapid geometric isomerization to **3a** and **3b** under reported[3,4] reaction conditions.[18,19]

The performance of the isomerization of **1c** as a solid-state reaction may be another reason for its remarkable stereoselectivity. If the first step, **1c** → **2c**, required only minimal molecular motions in the crystal[21] while the second step, **2c** → **3c**, involved extensive displacements in the lattice, the first step should be considerably kinetically preferred.

Acknowledgment. We are indebted to Dr. H.-D. Martin and Dr. J. Watthey for helpful comments on the manuscript.

Supplementary Material Available. A listing of structure factor amplitudes, fractional atomic coordinates, and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5007.

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(13) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).
(14) Crystals of **7** are: monoclinic; $P2_1$; $a = 6.684(2)$, $b = 10.391(3)$, $c = 8.355(2)$ Å; $\beta = 105.34(5)°$; $V = 559.6$ Å^3; $\rho_{calcd} = 1.33$ g cm^{-3} for $Z = 2$. Least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms on 938 independent reflections ($I \geq 2\sigma(I)$) converged at $R = 0.094$. A disorder in the crystal packing does not allow further refinement. However, the cis fusion of the oxirane ring in **7** is unequivocally established. See paragraph at end of paper regarding additional supplementary material.
(15) J. Ficini and A.-M. Touzin, *Bull. Chem. Soc. Fr.*, 2386 (1972).
(16) J. A. Berson, P. B. Dervan, and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 7598 (1972).
(17) Radical stabilization energy of the α-carbomethoxy group is about 4–4.5 kcal/mol relative to a hydrogen atom: (a) E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 4791 (1973); (b) H.-D. Martin and M. Hekman, *Chimia*, **28**, 12 (1974).
(18) Indeed, our preliminary experiments conducted in the molten state at lower temperature (105° rather than 140° reported in ref 4) show that **1b** isomerizes to a mixture of **2b** (60%) and **3b** (28%). **2b** can be isolated in pure form and gives Diels–Alder reactions similar to **2c**.
(19) The influence of the 1,4-substituents on the rates of cycloreversion in bicyclo[2.2.0]hexanes has been interpreted[17a,20c,e] in terms of formation of 1,4-biradical-like intermediates.[20] If, however, the cleavage of such a 1,4-biradical to a 1,5-diene were rate determining (as the thermal inversion of bicyclo[2.2.0]-*exo*-2,3,5,6-d_4-hexane appears to indicate[20b]), the direct comparison of molecules (*e.g.*, **1a–c**) with different substituents on *both* cleaving single bonds might be of limited value.
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(21) The torsional flexibility of the tricyclo[4.2.0.0^{2,5}]octane carbon skeleton (see ref 22 for **1a**) may preorientate, to some extent, the endocyclic single bonds for the ($\sigma 2_s + \sigma 2_a$) process.
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Daniel Belluš,* Hans-Christian Mez
Gretl Rihs, Hanspeter Sauter
Central Research Laboratories, Ciba-Geigy AG
4002 Basel, Switzerland
Received March 19, 1974

Carbon-13 Chemical Shifts of Amides and Imino Acid Residues. Effects of the Carbonyl Substituent and Syn–Anti Geometries

Sir:

Two well-separated ^{13}C resonances[1–5] have been reported for each C^β and C^γ ring carbon in peptides containing L-prolyl and hydroxy-L-prolyl (pyrrolidine) residues and have been assigned to the trans (I) and cis (II) isomers of the X-Pro[6] and X-Hyp peptide

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(2) K. Wüthrich, A. Tun-Kyi, and R. Schwyzer, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **25**, 104 (1972).
(3) D. E. Dorman and F. A. Bovey, *J. Org. Chem.*, **38**, 2379 (1973), and references therein.
(4) I. C. P. Smith, R. Deslauries, H. Saito, R. Walter, C. Garrigou-Lagrange, H. McGregor, and D. Sarantakis, *Ann. N. Y. Acad. Sci.*, **222**, 157 (1973).
(5) D. A. Torchia and J. R. Lyerla, Jr., *Biopolymers*, **13**, 97 (1974).
(6) Abbreviations: Pro = L-prolyl, Hyp = hydroxy-L-prolyl, X = any amino acid residue, Gly = glycyl, Ala = L-alanyl, Val = L-valyl, Sar = sarcosyl = *N*-methylglycyl.